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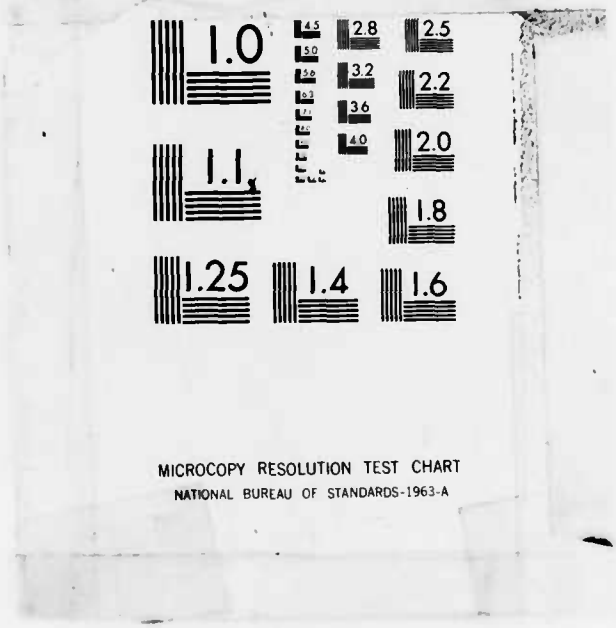
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CHEMICAL SYSTEMS LABORATORY

US Army Armament
Research and Development Command
Aberdeen Proving Ground, Maryland 21010

TECHNICAL REPORT
ARCSL-TR-83057

NONLINEAR LEAST-SQUARES FITTING OF FIRST-ORDER RATE COEFFICIENTS COMPARISON BETWEEN THE GAUSS-SEIDEL METHOD AND SWAIN'S KORE PROGRAM

by

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Chemical Branch
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June 1983

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-83057	2. GOVT ACCESSION NO. AD-A139080	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) NONLINEAR LEAST-SQUARES FITTING OF FIRST-ORDER RATE COEFFICIENTS. COMPARISON BETWEEN THE GAUSS-SEIDEL METHOD AND SWAIN'S KORE PROGRAM		5. TYPE OF REPORT & PERIOD COVERED 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Joseph W. Hovanec J. Richard Ward		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander/Chemical Systems Laboratory ATTN: DRDAR-CLB-CA Aberdeen Proving Ground, MD 21010		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161101A71A Research in Defense Systems
11. CONTROLLING OFFICE NAME AND ADDRESS Commander/Chemical Systems Laboratory ATTN: DRDAR-CLJ-IR Aberdeen Proving Ground, MD 21010		12. REPORT DATE June 1983 13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

First-order kinctics
Nonlinear, least-squares
Gauss-Seidel
KORE Program
LSKIN 1 Program

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Swain and coworkers at MIT recently composed a 92-statement Fortran computer program to evaluate first-order rate coefficients from kinctic data. The program is called KORE (kinetic analysis using overrelaxation); the use of the overrelaxation factor accelerates the convergence of the calculation which Swain feels would be of advantage for any equation fit with a least-squares method. To show the utility of the overrelaxation factor, Swain purposely used poor data to show that the KORE program converged while

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20. ABSTRACT (cont'd)

a much longer program by DeTar (LSKIN 1) did not converge.

At the Chemical Systems Laboratory (CSL), ~~we~~ have a general least-squares program based on the Gauss-Seidel method that was written in 1960 at Los Alamos Scientific Laboratory, and has been widely used in other laboratories based on the number of citations in the Science Citation Index. ~~We~~ thought that it might prove useful to see how this program handled the purposedly poor data Swain used to show the merit of the overrelaxation method. ~~We~~ found that the Gauss-Seidel program converged unlike DeTar's program, so it is uncertain what advantage the overrelaxation factor contributes for the general least-squares method.

Nevertheless, Swain's short program is still extremely useful for fitting first-order kinetic data with microcomputers, and Hovanec has adapted Swain's program in BASIC for the HP85 and APPLE II Plus computers.

PREFACE

This work was performed under Project 1L161101A71A, Research in Defense Sciences during FY83.

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NONLINEAR LEAST-SQUARES FITTING OF FIRST-ORDER RATE COEFFICIENTS (COMPARISON BETWEEN THE GAUSS-SEIDEL METHOD AND SWAIN'S KORE PROGRAM)

1. INTRODUCTION

Swain and coworkers at MIT[1] recently devised a 92-statement Fortran program, KORE (kinetic analysis using overrelaxation), to calculate first-order rate coefficients from kinetic data by least-squares fit of

$$y_t = a + be^{-kt} \tag{1}$$

where y_t = experimental point at t,

k = first-order rate coefficient,

t = time, and

a,b = constants.

Swain offers a number of advantages for KORE relative to other computer programs for evaluating first-order kinetic data. The KORE program has less than half the number of statements, can cope with almost any observed data, and does not require an initial estimate of k. In addition, convergence is accelerated by overrelaxation by a factor repeatedly re-evaluated by the program. Swain feels that his feature may be applicable to any iterative computer calculation.

To illustrate the capabilities of KORE, Swain supplied four data sets. One set uses actual experimental data, while three sets use intentionally poor data that Swain synthesized to test KORE against other programs. Swain noted that DeTar's least-square programs,[2] LSG or KSLIN 1, failed to converge with the artificial data.

At the Chemical Systems Laboratory (CSL), we have been using a general, nonlinear, least-squares program (LASL) written at Los Alamos Scientific Laboratory that is based on the Gauss-Seidel method.[3,4,5] Though this program has none of the advantages in size offered by KORE, the LASL program can be easily adapted to fit any equation, as long as one can take the first partial derivatives with respect to the parameters being fit. The widespread use of this program is indicated by the number of citations to Moore's report.[3] There were 93 citations between 1965-1969[6] and another 90 between 1970 and 1974,[7] the years for which cumulative indexes were available.

In order to compare the overrelaxation feature in KORE with the Gauss-Seidel method embodied in Moore's program, we tried Swain's data set in the LASL program.

2. EVALUATION OF FIRST-ORDER RATE COEFFICIENTS WITH MOORE'S PROGRAM

Consider the general function containing α parameters

$$y = f(x, \alpha_1 \ldots \alpha_m) \tag{2}$$

where y = dependent variable,

x = independent variable, and

α = parameter.

If the function is linear, one can find "best-fit" estimates of the parameters if one has n observations (n>m), by the usual least-squares method of minimizing

$$Q = \sum_{=1}^{n} \left\{ y_i - \left[f(x_{ij} \alpha_1 \ldots \alpha_m) \right] \right\} \tag{3}$$

The Gauss-Seidel method requires expansion of $f(x_i; \alpha_1 \ldots \alpha_m)$ in a Taylor's series around the point $(\alpha_{1,\phi} \ldots \alpha_{m,\phi})$ neglecting second-order and higher terms. Thus,

$$\Delta y_i = y_i - f(x_i; \alpha_{1,\phi} \cdots \alpha_{m,\phi})_6 = \sum_{=1}^{m} \frac{df}{d\alpha_j} \Delta\alpha_j \tag{4}$$

where $\frac{df}{d\phi j}$ is evaluated at the point $(\alpha_{1,\phi} \ldots \alpha_{m,\phi})$. Substitution of equation (4) into equation (2) means that standard linear multiple regression can be used regardless of the functional dependence of the parameters. Now Δy_i are the dependent variables, $df(x_i)/d\alpha_j$ are the independent variables, and one is trying to fit best-fit values of $\Delta\alpha_j$. Improved estimates of d_j are found by

$$\alpha_j = \alpha_{j,\phi} + h \, \Delta\alpha_j \tag{5}$$

where h is a constant, usually unity. The improved values of α_j are placed in equations (4) and (5), and the process repeated until the values of $\Delta\alpha_j$ are "sufficiently" small. In Moore's program that value is 10^{-6}.

For a first-order reaction, the function of interest[8] is

$$A_t = A_\infty + (A_o - A_\infty) \, e^{-kt} \tag{6}$$

where A_t = experimental point at time t,

A_o = experimental point at time zero,

A_∞ = experimental point at time infinity,

k = first order rate coefficient, and

t = time.

In agreement with Swain and with DeTar,[8] we also treat A_o and A_∞ as well as k as parameters to be fit. One can see that equations (1) and (6) are equivalent if $a = A_\infty$ and $b = (A_o - A_\infty)$. Swain[1] provides excellent rationale for the reasons for doing this as well as the reasons for finding k from equation (1) or equation (6), rather than taking the natural logarithm of equation (1) or equation (6) in order to get a linear equation.

Table 1 compares results from the KORE program and Moore's program using the "good" experimental data where one sees the best-fit parameters are precisely the same for each method. Moore's program required ten iterations for convergence.

Table 2 illustrates results for Moore's program with Swain's purposely poor data. The results show that Moore's program converged to the same values of k as obtained with the KORE program. Data set 2, which includes one late point, was the most difficult for Moore's program, requiring 26 iterations. For data set 3, by contrast, Moore's program converged in four iterations, in contrast to 13 for KORE. According to Swain, DeTar's program diverged with data sets 1 and 3, while the program was far from converging with data set 2 after 25 cycles.

Table 1. Comparison of KORE and Moore's Program with "Good" Experimental Data

Times	A,exp't	A,cal'd(Moore)	A,cal'd(KORE)
0.0	1.695	1.695	1.695
0.60	1.654	1.654	1.654
2.64	1.524	1.523	1.524
6.18	1.320	1.320	1.320
13.92	0.966	0.965	0.965
19.38	.774	.774	.774
26.94	.570	.570	.570
37.68	.368	.369	.369
84.12	.056	.056	.0556
107.34	.021	.021	.0211

	KORE	MOORE
A_o	= 1.695	1.695
A_∞	= 1.074	-1.074
k	= 0.04041 ± 0.000039[a]	0.04041 ± 0.000031[a]

[a]Standard deviation computed by respective programs as described in reference 1 for KORE and reference 3 for Moore.

We were also interested to see how the Gauss-Seidel method compared with DeTar's program. Reference 8 listed a sample fit of LSKIN 1 to some experimental data, so we used this data with Moore's program. Table 3 lists the results of that calculation. As one can see, the results are virtually identical.

One should keep in mind that the comparison between KORE and the Gauss-Seidel method relates solely to the utility of the overrelaxation factor, in view of the failure of DeTar's program to converge when KORE did. Moore's program is useful as a general least-squares program that can be easily adapted to any function, while Swain's program is restricted to first-order kinetics. For anyone who needs a program for analyzing first-order kinetics, KORE is an excellent choice. KORE is particularly useful with personal computers and has been converted into BASIC for the HP85 and Apple II Plus.

Table 3. Comparison Between LSKIN 1 and Gauss-Seidel Method

Times	%T,[a] exp't	%T, cal'd(LSKIN 1)	%T,[b] cal'd(Moore)
1.0	91.2	92.2	92.2
4.0	79.7	79.7	79.7
7.0	69.6	69.3	69.3
10.	61.3	60.7	60.7
13.	54.0	53.5	53.5
16.	47.6	47.5	47.5
19.	42.4	42.4	42.4
22.	37.9	38.0	38.0
25.	34	34.3	34.3
28.	31	31.1	31.1
31.	28	28.3	28.3
34.	26	25.9	25.9
37.	23.9	23.8	23.8
40.	21.6	22.0	22.0
43.	20.8	20.4	20.4

	DeTar (LSKIN 1)	Gauss-Seidel
T_o	97.0	97.0
T_∞	4.61	4.65
k	0.0168	0.0168

[a]Percent transmittance

[b]Experimental values of percent transmittance were converted to absorbance and fit with equation (6) after which they were converted back to percent transmittance for comparison with LSKIN 1.

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